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THE STRUCTURE OF XANTHALIN

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We have previously isolated from the roots of Xanthogalum purpurascens Lallem two acylcoumarins—ostruthol [1] and xanthogalin [2, 3]. Continuing our study of this plant it has been found that the composition of the lactones in it differs according to the growth site. Whether this is a consequence of a nonuniformity of the species or of the influence of external conditions has not yet been determined.

From the raw material prepared by M. G. Pimenov in the Transcaucasus we have isolated a new coumarin $C_{24}H_{26}O_7$ with mp 111–113° C, $[\alpha]_D^{20}$ −164.2° (c 0.97; ethanol), readily soluble in organic solvents and insoluble in water. This possessed chemical properties characteristic for lactones of the coumarin group (lactone test, reaction with diazotized sulfanilamide).

From its UV spectrum (the positions of the absorption bands and the ratios of their intensities), it had the coumarin skeleton. A small peak in the 258 mμ region (log ε 3.48) permitted the assumption that the substance has the structure of a dihydrofuro- or dihydropyranocoumarin (Fig. 1).

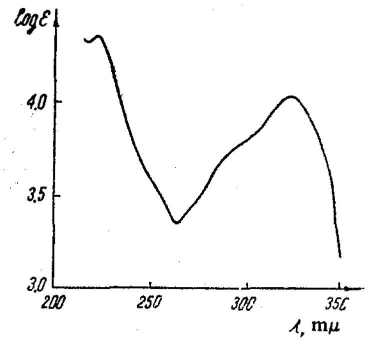


Fig. 1. UV spectrum of xanthalin (solution in ethanol).

The IR spectrum of the coumarin (Fig. 2) had absorption bands specific for coumarins: 1740–1718 cm^{-1} (CO of α-pyrone ring), 1633 and 1570 cm^{-1} (aromatic nucleus). The broad carbonyl bands show the possibility of the presence of an ester grouping in the lactone, and this was confirmed by the change in the R_f value when the substance was treated with caustic alkali. Judging from its physicochemical constants, the coumarin that we have isolated is a new acylcoumarin, and we have given it the name of xanthalin.

The structure of xanthalin was established on the basis of its NMR spectrum (Fig. 3).

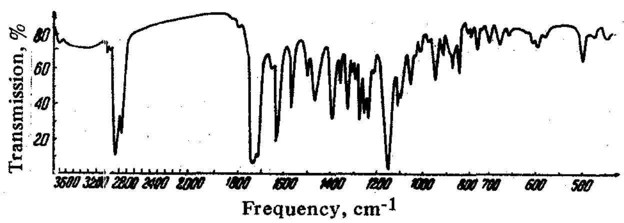
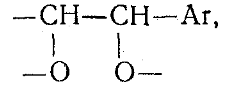


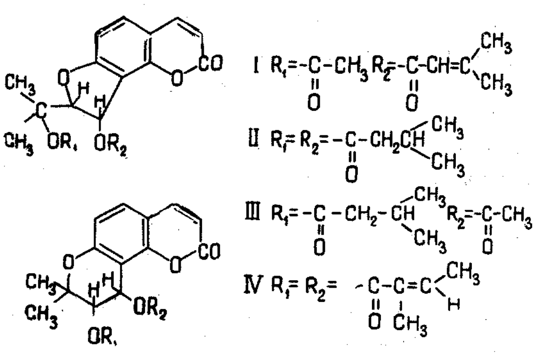
Fig. 2. IR spectrum of xanthalin (mull in oil).

Doublets a and e (δ = 7.62 and 6.28, J = 10 Hz) together with the singlets b (δ = 7.36) and c (δ = 6.79) characterize xanthalin as a 6,7-disubstituted coumarin [4]. The doublets d (δ = 6.34, J = 4.5 Hz) and g (δ = 5.52, J = 4.5 Hz) relate to the two interacting protons in the



$$-\underset{\substack{|\\-O}}{CH}-\underset{\substack{|\\O-}}{CH}-Ar,$$

group, where Ar is an aromatic radical. A similar quadruplet is found in the spectra of dihydrofuro- and dihydropyrano- coumarins with two acyl residues attached to the dihydrofuran or dihydropyran ring: peucenidin (I), athamantin (II), dihydrosamidin (III), anomalin (IV), and others.



Peaks h, i, and j show that the xanthalin molecule has two angelic acid residues. The doublet h (δ = 2.03, J = 7 Hz) is due to the methyl group in the β-position of one of the acid residues. The cause of the weak splitting of each of the components of the doublet (J = 1 Hz) is apparently a homoallyl interaction with the protons of the α-methyl group. The broadened peak with complex splitting i (δ = 1.86) appears as the result of the superposition of the signal from the α-methyl group of the first residue and one of the components of the doublet of a β-methyl group, analogous to h. The second component of this doublet, having fused with the signal from the other α-methyl group, gives peak j (δ = 1.78). The difference in the positions of the signals of the methyl groups of the acid residues is obviously connected with features of their spatial arrangement in the molecule. The vinyl protons of the acid residues give the very broad signal *f* [5]. The singlets k (δ = 1.46 and 1.49) are due to the protons of two nonequivalent methyl groups on carbon atom 4.

The assignments made are fully confirmed by the ratio of the integral intensities of the signals considered.

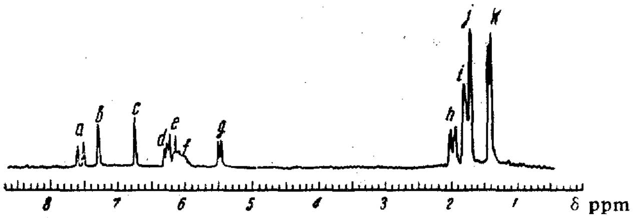
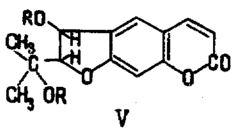
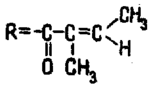


Fig. 3. NMR spectrum of xanthalin.

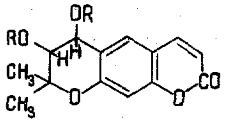
The spectrum discussed may correspond to two variants of the structure of xanthalin—(V) or (VI).



V



$R = -\underset{O}{\overset{\|}{C}}-\underset{CH_3}{C}=C\begin{smallmatrix}CH_3\\ H\end{smallmatrix}$



VI

The choice between these variants was made on the basis of the considerations that we have used previously in the study of the structures of xanthogalol and zosimol [3].

For compound (V), the signals of the methyl groups must be located in a weaker field than for compound (VI) because of the electron-accepting influence of the ester grouping. Below, we give the values of the chemical shifts of the protons of the methyl groups of compounds with a known structure, which are in complete harmony with those proposed by us.

Compound	Chemical shifts of the protons of the methyl groups
Peucenidin (I)	1.65; 1.74
Athamantin (II)	1.63; 1.74
Dihydrosamidin (III)	1.41; 1.44
Anomalin (IV)	1.46; 1.50
Xanthalin	1.46; 1.49

Consequently, the methyl signals in the NMR spectrum of xanthalin are located at the same interval of values of the chemical shifts as the signals in the spectra of the dihydropyranocoumarins dihydrosamidin and anomalin; the signals from the protons of the methyl groups of dihydrofurocoumarins are in the region of weaker fields. Thus, it may be concluded that xanthalin has the structure (VI).

Experimental

Isolation of xanthalin. Two kilograms of the dried and comminuted roots of the Xanthogalum was extracted three times with methanol (12, 7, and 5 *l*). The extract was concentrated in vacuum to a volume of 0.5 *l*, 1 *l* of water was added, and the mixture was extracted with diethyl ether (3 × 250 ml). The solvent was driven off from the ethereal extracts (residue 97.75 g). The residue obtained (30 g) was dissolved in 30 ml of benzene and chromatographed on a column of acidic alumina 14 cm high and 8 cm in diameter. The column was eluted with thiophene-free benzene. The first fraction, fluorescing violet in ultraviolet light (500 ml), was concentrated to small bulk. On standing, colorless needle-like crystals associated into nodules with mp 111–113° C (from petroleum ether and methanol) deposited. Yield 0.56 g; UV spectrum λ_{max} 222, 258, 323 mμ (log ε 4.36, 3.48, 4.03); IR spectrum (mull in paraffin oil): 1740–1718 cm^{-1}, 1633, 1570, 1470, 1388, 1321, 1270, 1235, 1150 cm^{-1}.

Found, %: C 67.65, 67.87; H 6.08, 6.08; mol. wt. 430 (Badger-Rast isothermal method in ether). Calculated for $C_{24}H_{26}O_7$, %: C 67.60; H 6.10.

The IR spectra were taken on a UR-10 spectrograph, the UV spectra on an SF-4 spectrometer (solution in ethanol), and the NMR spectra on a JNM-4H-100 spectrometer. The microanalysis was performed by E. A. Nikonova.

Conclusions

From the roots of Xanthogalum purpurascens growing in the Transcaucasus, we have isolated a new coumarin, $C_{24}H_{26}O_7$ with mp 111–113° C, $[\alpha]_D^{20}$ −164.2° (c 0.97; ethanol) which we have called xanthalin. On the basis of the NMR spectrum it has been established that xanthalin is 3',4'-diangeloyl-2',2'-dimethyl-3',4'-dihydropyrano-5',6':6,7-coumarin.

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